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Formulation and Implementation of Frequency-Dependent Linear Response Properties with Relativistic Coupled Cluster Theory for GPU-Accelerated Computer Architectures

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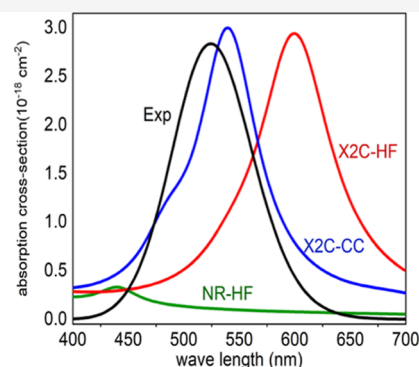
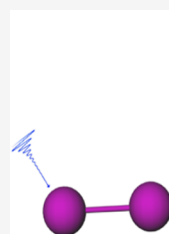


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ABSTRACT: We present the development and implementation of relativistic coupled cluster linear response theory (CC-LR), which allows the determination of molecular properties arising from time-dependent or time-independent electric, magnetic, or mixed electric-magnetic perturbations (within a common gauge origin for the magnetic properties) as well as taking into account the finite lifetime of excited states in the framework of damped response theory. We showcase our implementation, which is capable to offload the computationally intensive tensor contractions characteristic of coupled cluster theory onto graphical processing units, in the calculation of (a) frequency-(in)dependent dipole–dipole polarizabilities of IIB atoms and selected diatomic molecules, with a particular emphasis on the calculation of valence absorption cross sections for the I_2 molecule; (b) indirect spin–spin coupling constants for benchmark systems such as the hydrogen halides (HX, X = F–I) as well the H_2Se-H_2O dimer as a prototypical system containing hydrogen bonds; and (c) optical rotations at the sodium D line for hydrogen peroxide analogues (H_2Y_2 , Y = O, S, Se, Te). Thanks to this implementation, we are able to show the similarities in performance, but often the significant discrepancies, between CC-LR and approximate methods such as density functional theory. Comparing standard CC response theory with the flavor based upon the equation of motion formalism, we find that for valence properties such as polarizabilities, the two frameworks yield very similar results across the periodic table as found elsewhere in the literature; for properties that probe the core region, such as spin–spin couplings, on the other hand, we show a progressive differentiation between the two as relativistic effects become more important. Our results also suggest that as one goes down the periodic table, it may become increasingly difficult to measure pure optical rotation at the sodium D line due to the appearance of absorbing states.



1. INTRODUCTION

The fundamental molecular properties that are connected to the response of a system to external perturbations, such as electric or magnetic fields, are central to the study of linear and nonlinear optics.^{1–4} It is widely acknowledged that molecules containing heavy elements, that is, those found toward the lower parts of the periodic table, have a plethora of applications. For instance, by manipulating the molecular polarizability, researchers can design materials with advanced optical properties for use in photovoltaic devices and glasses, such as bismuth oxide-based materials.⁵ Another important example is the utilization of optical activity to design lanthanide complexes as chiral probes for biological processes.⁶ A detailed understanding of the physical phenomena behind these properties at the atomic or molecular level is very important to tune them or to provide insights into the development of new materials and novel applications.

In quantum mechanics, molecular properties can be derived via perturbation theory or, more specifically, through the

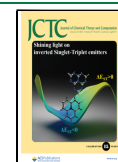
response theory formalism, which, in general, identifies molecular properties from the derivatives of the energy (or an equivalent quantity) with respect to the external perturbations. The genesis of modern response theory may perhaps be traced back to the introduction by Langhoff et al.⁷ in 1972 of a formalism that allowed both time-dependent and time-independent perturbations to be taken into account analytically, that is, without employing finite-difference (finite-field) approaches, which are numerically straightforward (but computationally expensive) and only applicable to the time-independent case. Among the properties one can calculate, those

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related to the linear response^{8,9} of the systems are particularly interesting since they give rise to, for example, polarizability and optical activity and can provide us with information on electronically excited states.

The current formulations of response properties may be categorized into those employing either Ehrenfest theorem^{10,11} or quasi-energy approaches.^{12–14} Although response theory based on exact wave functions can provide the expressions for molecular properties directly, practical applications require the use of approximate models such as Hartree–Fock (HF) and density functional theory (DFT), and many other wave function-based approaches such as multiconfiguration self-consistent field, configuration interaction (CI), and coupled cluster (CC), to name just a few (see Helgaker et al.⁹ for a comprehensive survey). To date, response theory has achieved great success in dealing with a wide variety of molecular properties and treating both small and large-scale systems.^{8,9,15–18} Here, the availability of analytic derivative approaches has proven to be important for efficient calculations, particularly for large-scale molecule simulations.

However, while most formulations (and implementations) of response theory mentioned above are based on nonrelativistic quantum mechanics, it is now widely recognized that when dealing with molecules containing heavy elements, relativistic effects must also be taken into account.^{19–22} In addition, heavy elements also have more electrons than their lighter counterparts, which can bring about subtler effects due to electron correlation that may significantly impact the molecular properties. In the domain of relativistic quantum chemistry, the linear-response function based on approximate models including HF,^{23,24} DFT,^{25,26} and second-order-polarization-propagator approximation²⁷ has been well established. Due to its modest computational cost, DFT has become the most widely used approach for correlated electronic structure theory, even though it is not possible to systematically improve the quality of calculations with currently available density functional approximations.²⁸ Due to that, depending on the property of interest, DFT results may deviate strongly from experimental or accurate theoretical models for relativistic electronic structure calculations, even for closed-shell species around the ground-state equilibrium structure.^{29,30} An alternative to DFT is found in CC theory, which is considered a “gold standard”^{31,32} among electronic structure methods due to its ability to yield results that approach chemical accuracy for both correlation energies and properties.

To date, there are various CC linear-response (CC-LR) implementations based on standard models such as CC2,³³ CCSD^{14,15} and CC3.³⁴ These approaches have been shown to achieve good agreement with experimental values for both electric and magnetic molecular properties.^{35–40} We also note the emergence in recent years of response theory implementations based on the equation-of-motion coupled cluster (EOM-CC) model,^{41–46} which are appealing due to their simpler programmable expressions while yielding exactly the same excitation energies as CC-LR and nearly equivalent numerical results for response properties. In the time-dependent framework, as pointed out by Coriani et al.,⁴¹ the EOM-CC response is equivalent to the combination of an exponential parametrization for the ground-state wave function and a linear parametrization for the time-dependent wave function (which these authors refer to as a CC–CI type wave function), as opposed to the CC-LR case, which employs exponential parametrizations for both time-dependent and time-independ-

ent wave functions (referred to as CC–CC type wave functions).

A significant downside of these implementations, however, is that they are available only for nonrelativistic or, rather, approximate relativistic Hamiltonians. As such, they are not generally suitable for treating molecular systems containing heavy elements. In this manuscript, we aim to bridge this gap and present the implementation and pilot applications of CC-LR and EOM-CC models in combination with relativistic Hamiltonians as a part of the ExaCorr⁴⁷ module of the DIRAC program.⁴⁸ One feature of ExaCorr is its ability, through the use of the ExaTENSOR⁴⁹ library, to carry out distributed tensor operations with offloading to graphical processing units (GPUs), which have been shown to be ideally suited to accelerate coupled cluster calculations due to the latter's substantial floating-point operation and memory-intensive nature.^{47,50–53} In the work detailed here, we take advantage of GPU offloading and thread-level parallelism and will discuss the currently ongoing work to enable large-scale parallel calculations in a subsequent publication.

Apart from discussing our implementation, we showcase its generality and versatility by examining examples of three distinct classes of molecular properties: those involving purely electrical perturbations, purely magnetic perturbations, and mixed electric and magnetic perturbations.

As an example of the first class, we take the electric dipole polarizabilities into account because of their significance in a wide range of applications and because they provide valuable insights into the properties and behavior of molecules. For example, materials with high dipole polarizabilities and dielectric constants are used in the polymers that are needed for high-energy-density capacitors,⁵⁴ while materials with low dipole polarizabilities⁵⁵ are used as insulators in electrical devices. For optical spectroscopies, in the calculation of resonant processes such as electronic excitations, it is important, from both practical and physical points of view, to account for the finite excited-state lifetimes in the calculation of response functions since these will relate to the broadening in the measured spectra. The damped coupled cluster response theory has, in recent years, emerged as a very effective tool for incorporating such effects in simulating the spectroscopy of complex molecules.^{56–60} In this article, we demonstrate our ability to calculate damped response functions, as we can handle perturbing external fields with either real or complex frequencies.

We consider indirect nuclear spin–spin coupling constants to be representative of the second class. Indirect nuclear spin–spin coupling constants manifest themselves in nuclear magnetic resonance (NMR) spectroscopy, which, alongside optical spectroscopies, is another invaluable tool in chemistry. As a substantial fraction of the atoms in the periodic table is NMR-active, the technique can very often be used to provide critical information about their chemical environment^{61–63} in a nondestructive way. Regarding computational analysis, apart from the fact that theoretical calculations are extremely useful to interpret experimental signals, it has been demonstrated that it is essential to account for relativistic effects already for elements around the third row of the periodic table.^{64–68} Magnetic properties are often challenging to calculate due to the dependence of the results on the gauge origin of an external magnetic field for incomplete bases sets. However, the indirect spin–spin coupling is expressed as the second derivative of the electronic energy with respect to the internal magnetic fields caused by nuclear spins, so the gauge-origin issue does not arise.

Optical rotation is taken as an example of the third class. Studying optical rotation is of significant interest for several reasons. First and foremost, optical rotation measurements can provide information about the chiral nature of molecules. This is particularly important in the pharmaceutical industry, as many drugs are chiral and their properties can vary depending on their handedness.⁶⁹ In addition to its applications in the pharmaceutical industry, studying optical rotations can also provide insights into the electronic and structural properties of molecules. Optical rotations are influenced by a variety of factors, including the electronic structure of the molecule, the molecular geometry, and the surrounding environment. Moreover, in materials science, the optical properties of materials can be used to design and develop new materials.⁷⁰ For this property, the gauge-origin issue mentioned above also arises.⁹ In subsequent work, we will explore approaches to ensure gauge-invariance for coupled-cluster calculations of optical rotation,^{71–73} but we note that for the small, symmetric molecules studied here, the use of a common gauge origin yields sufficiently accurate results to allow for a comparison of different electronic structure approaches,^{74–76} which is our goal here.

The manuscript is organized as follows: in Section 2, response theory and its corresponding parametrization for the time-dependent coupled cluster wave function are summarized. In Section 3, we described the details of the implementation. Section 4 is devoted to the details of the computations we used to test the implementation. The calculations are presented and discussed in Section 5. Finally, a brief summary is given in Section 6.

2. THEORY

We base the theory on the time-averaged quasienergy formalism, which we briefly summarize below, and refer the reader to the landmark paper by Christiansen et al.¹⁴ for a detailed discussion on it, as well as other more recent works.^{15,16,41}

2.1. Response Functions Based on Time-Average Quasienergy. We aim to solve the time-dependent wave equation

$$i\frac{\partial}{\partial t}|\Psi(t)\rangle = H|\Psi(t)\rangle \quad (1)$$

where H is the total electronic Hamiltonian

$$H = H_0 + V(t) \quad (2)$$

composed of H_0 , which represents the time-independent electronic Hamiltonian (e.g., the Dirac–Coulomb (DC) Hamiltonian, the eXact 2-component Hamiltonian (X2C), the Levy-Leblond Hamiltonian, and so forth, see refs 20 and 48 and references therein), and $V(t)$ representing a sum of N perturbations that are periodic in time with frequencies ω_k

$$V(t) = \sum_{k=1}^N [(e^{i\omega_k t} + e^{-i\omega_k t}) \sum_x \epsilon_x(\omega_k) X] \quad (3)$$

expressed in terms of a one-body operator X and the associated frequency-dependent perturbation strength $\epsilon_x(\omega_k)$. In the present study, X corresponds, for instance, to the x -component of the electric dipole operator $\hat{\mu}_x$, or to the y -component of the magnetic dipole operator, \hat{m}_y , and so forth.

According to the time-averaged, time-dependent Hellmann–Feynman theorem,^{7,14} by defining a time-averaged quasienergy $\{Q\}_T$ (over the period T)

$$\{Q\}_T = \frac{1}{T} \int_{-T/2}^{T/2} \left\langle 0(t) \left| \left(\hat{H} - i\frac{\partial}{\partial t} \right) \right| 0(t) \right\rangle dt \quad (4)$$

and making it stationary to changes in $|0(t)\rangle$, we arrive at a definition of time-dependent response properties as derivatives of $\{Q\}_T$

$$\{Q\}_T = E_0 + \sum_x \langle X \rangle \epsilon_x(0) + \frac{1}{2} \sum_{x,y,k} \langle \langle X; Y \rangle \rangle_{\omega_k} \epsilon_y(\omega_k) \delta(\omega_0 + \omega_k) \quad (5)$$

where

$$\langle X \rangle = \frac{d\{Q\}_T}{d\epsilon_x(0)} \quad (6)$$

corresponds to an expectation value and

$$\langle \langle X; Y \rangle \rangle_{\omega_k} = \frac{d^2\{Q\}_T}{d\epsilon_x(\omega_0) d\epsilon_y(\omega_k)}, \quad \omega_0 = -\omega_k \quad (7)$$

to linear response properties.

2.2. Parametrization of the Time-dependent Wave Function. In the following, we shall be concerned with wave functions based on an exponential parametrization of the ground state wave function, such as the coupled cluster expansion

$$|0\rangle = e^{T_0}|R\rangle = |CC\rangle \quad (8)$$

in which $|R\rangle$ denotes the reference state, typically the HF wave function, and T_0 is the time-independent cluster operator, here restricted to single (ν_1) and double (ν_2) excitations

$$T_0 = T_1 + T_2 = \sum_{\nu_1} t_{\nu_1} \hat{t}_{\nu_1} + \sum_{\nu_2} t_{\nu_2} \hat{t}_{\nu_2} = \sum_{ai} t_i^a \{a_a^\dagger a_i\} + \frac{1}{4} \sum_{abij} t_{ij}^{ab} \{a_a^\dagger a_b^\dagger a_j a_i\} \quad (9)$$

with a and b indicating particle lines and i and j hole lines, respectively,³¹ and ν_1 and ν_2 representing excited configurations with respect to the reference ($\nu_1 \leftrightarrow |l_i^a\rangle = \{a_a^\dagger a_i\}|R\rangle$, $\nu_2 \leftrightarrow |l_{ij}^{ab}\rangle = \{a_a^\dagger a_b^\dagger a_j a_i\}|R\rangle$); in the following, we shall sometimes omit explicit excitation ranks and particle/hole labels and instead employ the shorthand notation μ, ν to denote excited determinants.

As suggested by Pawłowski et al.,¹⁵ the time-dependent wave function $|0(t)\rangle$ can be parametrized in a general manner as

$$|0(t, \epsilon_x)\rangle = e^{B_0} e^{B(t, \epsilon_x)} |R\rangle \quad (10)$$

where e^{B_0} and $e^{B(t, \epsilon_x)}$ define the parametrization of the time-independent and time-dependent wave functions associated with perturbation X with perturbation strength ϵ_x , respectively. In the case of coupled cluster wave functions, $B_0 = T_0$, the choice to be made is that of the parametrization of the time-dependent part. If the exponential parametrization is retained, we have the CC–CC model (more commonly known as LR–CC), whereas for a linearized version we have the CC–CI model (also referred to as EOM–CC)

$$e^{B(t, X)} \simeq 1 + B(t, \epsilon_x) = 1 + \sum_{ai} t_i^a(t, \epsilon_x) \{a_a^\dagger a_i\} + \frac{1}{4} \sum_{abij} t_{ij}^{ab}(t, \epsilon_x) \{a_a^\dagger a_b^\dagger a_j a_i\} \quad (11)$$

2.3. Coupled Cluster Linear Response Function. As in the time-independent case, the nonvariational nature of the coupled cluster method requires that we define a second-order quasienergy Lagrangian

$$\{L\}_T = \{Q\}_T + \sum_{\mu} \bar{t}_{\mu}^{(0)} \left\langle \left\langle \bar{\mu} \left| e^{-B^{(1)}(t, \epsilon_x)} \left(H - i \frac{\partial}{\partial t} \right) e^{B^{(1)}(t, \epsilon_x)} \right| CC \right\rangle \right\rangle_T \quad (12)$$

in order to obtain the linear response functions. Here, $\langle \bar{\mu} | \equiv \langle \mu | e^{-T_0}$ and $\bar{t}_{\mu}^{(0)}$ are the Lagrange multipliers for the ground-state obtained solving the linear system

$$\bar{\mathbf{t}}^{(0)} \mathbf{A} = -\boldsymbol{\eta} \quad (13)$$

in which the matrix \mathbf{A} is the Jacobian matrix. We note that \mathbf{A} is strictly equivalent to the normal-ordered, similarly transformed Hamiltonian \bar{H}_N

$$A_{\mu\nu} \equiv (\bar{H}_N)_{\mu\nu} = [\exp(-\hat{T}_0) \hat{H}_0 \exp(\hat{T}_0) - \langle \text{HF} | \hat{H}_0 | \text{HF} \rangle] \quad (14)$$

In the following, we shall use the two terms interchangeably and, for brevity, drop the subscript N in \bar{H}_N .

The linear response functions are expressed as

$$\text{CC-CC} \langle \langle X; Y \rangle \rangle_{\omega_k} = \frac{1}{2} C^{\pm\omega} P(X(\omega_0), Y(\omega_k)) \left[\boldsymbol{\eta}^X + \frac{1}{2} \mathbf{F} \mathbf{t}^X(\omega_0) \right] \mathbf{t}^Y(\omega_k) \quad (15)$$

for CC-CC^{14,15,41} and

$$\text{CC-CI} \langle \langle X; Y \rangle \rangle_{\omega_k} = \frac{1}{2} C^{\pm\omega} P(X(\omega_0), Y(\omega_k)) \left[\text{EOM} \boldsymbol{\eta}^X \mathbf{t}^Y(\omega_k) - \sum_{\mu} \bar{t}_{\mu}^{(0)} \mathbf{t}_{\mu}^X(\omega_0) \sum_{\nu} \bar{t}_{\nu}^{(0)} \boldsymbol{\xi}_{\nu}^Y \right] \quad (16)$$

for CC-CI.^{15,41,46} In the equations above, $P(X(\omega_0), Y(\omega_k))$ acts to permute perturbations X and Y , and

$$C^{\pm\omega} f^{XY}(\omega_0, \omega_k) = f^{XY}(\omega_0, \omega_k) + f^{XY}(-\omega_0, -\omega_k)^* \quad (17)$$

symmetrizes the response functions with respect to simultaneous complex conjugation and inversion of the sign of the frequencies.¹⁴

We have also implemented an alternative expression for the response function, which can be rewritten in an asymmetric form¹⁴

$$\text{CC-CC} \langle \langle X; Y \rangle \rangle_{\omega_k} = \frac{1}{2} [\boldsymbol{\eta}^X \mathbf{t}^Y(\omega_k) + \bar{\mathbf{t}}^Y(\omega_k) \boldsymbol{\xi}^X] \quad (18)$$

where $\bar{\mathbf{t}}^Y$ collect the derivatives of Lagrange multipliers with respect to one perturbation. The asymmetric form gives the same results as the symmetric form and has advantages in some cases, such as NMR calculations⁷⁷ as one needs to solve response equations for one operator (e.g., Y), but at the cost of having to solve response equations for both perturbed amplitudes and multipliers. In the properties investigated in this manuscript, the asymmetric form does not offer a clear advantage, and as such, we focus on the symmetric form in the following.

To evaluate the linear response function, we need to obtain the frequency-(in-)dependent first-order perturbed amplitudes \mathbf{t}^Y by solving the corresponding first-order right-hand side response equations¹⁴

$$(\bar{\mathbf{H}} - \omega_k \mathbf{I}) \mathbf{t}^Y = -\boldsymbol{\xi}^Y \quad (19)$$

with \mathbf{I} as the identity matrix.

Because of the equivalence between \mathbf{A} and $\bar{\mathbf{H}}$, eq 19 is the same for the CC-CC and CC-CI models, and the poles of the response functions will occur at the same places in the two formulations. This is in line with the fact that the excitation energies for CC-LR and EOM-CC are the eigenvalues of \mathbf{A} or $\bar{\mathbf{H}}$, respectively.

Here, we use the same definitions for matrices $\boldsymbol{\eta}^Y$, $\boldsymbol{\xi}^Y$, and \mathbf{F} (the coupled cluster Hessian) as done by Christiansen et al.,¹⁴ which are listed in Table 1, and note that in the case of CC-CI,

Table 1. Vectors and Matrices for the CC Linear Response Function^a

$\boldsymbol{\eta}^Y$	$\langle \text{Al} Y, \hat{t}_{\mu} \text{CC} \rangle$
$\boldsymbol{\xi}^Y$	$\langle \bar{\mu} Y \text{CC} \rangle$
\mathbf{F}	$\langle \text{Al} [H_0, \hat{t}_{\mu}], \hat{t}_{\nu} \text{CC} \rangle$
\mathbf{A}	$\langle \bar{\mu} [H_0, \hat{t}_{\mu}] \text{CC} \rangle$

^a $|\text{CC}\rangle = e^{T_0} |R\rangle$ denote the regular CC reference wave function, and $|R\rangle$ is the reference state for the CC parametrization such as the HF state. $\langle \text{Al} | = \langle R | + \sum_{\mu} \bar{t}_{\mu}^{(0)} \langle \bar{\mu} |$. $\langle \bar{\mu} | = \langle R | \hat{t}_{\mu}^{\dagger} e^{-T_0} \equiv \langle \mu | e^{-T_0}$, where \hat{t}_{μ}^{\dagger} is the deexcitation operator, which is biorthogonal to the excitation operator \hat{t}_{μ} , satisfying $\langle R | \hat{t}_{\mu}^{\dagger} \hat{t}_{\nu} | R \rangle = \delta_{\mu\nu}$.

$\boldsymbol{\eta}^Y$ is replaced by $\text{EOM} \boldsymbol{\eta}^Y$, as defined by Faber and Coriani.⁴⁶ The detailed working equations used in our implementation are listed in the Supporting Information.

Finally, due to the fact that ExaCorr was originally designed for treating systems without symmetry and that, in such a case, the relativistic wave functions are complex-valued, complex algebra is used throughout. This makes the implementation of damped coupled cluster response theory relatively straightforward; it suffices, in the computation of the response function of interest (for instance, the yy component of the electric dipole polarizability, $\alpha_{yy}(\omega_0; \omega_k)$), to set the imaginary component of the perturbing frequency ω_k to a particular inverse lifetime γ

$$\omega_k \equiv \omega_k + i0 \rightarrow \omega_k + i\gamma \quad (20)$$

when solving the response equation^{56–58}

$$(\bar{\mathbf{H}} - (\omega_k + i\gamma) \mathbf{I}) \mathbf{t}^Y(\omega_k + i\gamma) = -\boldsymbol{\xi}^Y \quad (21)$$

subject to the condition that $(\omega_k + i\gamma) + (-\omega_0 - i\gamma) = 0$. We note that while we can in principle use a different value of γ for each ω_k , in practice, we will follow common usage and keep this value constant for a range of frequencies for which we shall calculate a particular response function. With that, the absorption cross-section for dipole transitions can be determined by the imaginary part of the complex electric dipole polarizability⁷⁸

$$\sigma(\omega) = \frac{4\pi\omega}{c} \text{Im}[\bar{\alpha}(\omega)] \quad (22)$$

3. IMPLEMENTATION

The above-mentioned algorithm has been implemented in the development version of the relativistic quantum chemistry package DIRAC⁴⁸ as a part of the ExaCorr code.⁴⁷ Currently, the implementation allows for calculations to be carried out only by using a single-node configuration. The implementation of multinode is currently in progress and will be reported in

forthcoming works. We can summarize the main computational tasks in the following four steps:

1. Solve the closed-shell ground-state CCSD equations to obtain the \mathbf{t}_1 and \mathbf{t}_2 amplitudes.
2. With \mathbf{t}_1 and \mathbf{t}_2 , construct the one- and two-body intermediates that are necessary for building the $\bar{\mathbf{H}}$ and linear response functions.
3. Solve the linear response equation in the full single–double excitation space to obtain the first-order perturbed amplitudes for each operator–frequency combination. To avoid the explicit construction of a large matrix $\bar{\mathbf{H}}$, an iterative solver is employed.
4. Construct the response function by combining the first-order perturbed amplitudes and the property integrals in the molecular orbital (MO) basis.

The first step is carried out within a Kramers-unrestricted formalism⁷⁹ and has been extensively discussed in prior work.⁴⁷

The intermediates in the second step consist of two sets: the first set is property-independent and is utilized to construct the σ -vectors, which are the projections of $\bar{\mathbf{H}}$ in the trial vector space. These intermediates were previously discussed in the literature^{80,81} and an implementation of relativistic EOM-CC is available in the RelCCSD module⁸² as well. We have included a rewritten version of the σ -vectors for EOM-CC for excitation energies (EOM-EE) in the Supporting Information (for completeness, expressions for the left EOM-EE σ -vectors are also given) due to our use of full tensors in this implementation. We have also corrected misprints identified in the expressions given by Shee et al.⁸² (the previously implemented expressions were verified and found to be correct).

In deriving the working equations, we note that for the matrix \mathbf{F} , it is not possible to obtain its matrix elements diagrammatically⁸³ due to the number of unconnected hole/particle-lines. However, \mathbf{F} is never used by itself but rather as the vector-matrix product $\mathbf{t}^X \mathbf{F}$, in analogy to the σ -vector expressions for the eigenvalue and response equations. Apart from being readily expressed diagrammatically, dealing with the vector-matrix product is computationally advantageous as it reduces storage requirements.

Moreover, as Faber and Coriani⁴⁶ suggested, we can avoid computing the \mathbf{F} matrix in CC–CI implementation by computing the ${}^{\text{EOM}}\eta^X$, which is easily accomplished by modifying the existing η^X routine (see working equation in the Supporting Information).

In the current implementation, the set of all property-related intermediates is computed on the MO basis, but as the property integrals are first generated on the atomic orbital (AO) basis in DIRAC, it is necessary to transform all desired property integrals from AO to MO prior to the response calculations. All the intermediates and the property integrals in MO basis are therefore stored as tensor objects according to the definition of the TAL-SH library,⁸⁴ so that they can be efficiently employed in constructing the elements of ξ^X , η^X , and ${}^{\text{EOM}}\eta^X$.

In the Supporting Information, we will focus on discussing the third step, which involves solving the first-order response equation. There are different algorithms to solve linear equations, such as direct inversion of the iterative subspace,^{85–87} as well as the Lanczos-chain^{59,88} and Davidson⁸⁹ schemes. In the current work, we utilized the latter, which required minor modifications with respect to evaluating the eigenvalues and eigenvectors of $\bar{\mathbf{H}}$ in our EOM-CC implementation. We also note that the default algorithm in ExaCorr to solve for the

unperturbed amplitudes \mathbf{t} was recently changed to conjugate residual with OPTimal trial vectors (CROP)^{90,91} as this reduces the memory requirements in this stage of the calculation.

One particular difference between our implementation and the one by Shee et al.⁸² is that the ExaTENSOR and TAL-SH libraries, for reasons of scalability and generality, do not enforce triangularity or the (anti)symmetry of tensors with respect to the exchange of pairs of indices. Consequently, and in contrast to the prior implementation, beyond rank-2 tensors, antisymmetry needs to be enforced in order to ensure that, at all times, we satisfy the underlying Fermionic nature of the problem.

For example, in the generation of trial vectors for the \mathbf{t}_2^X amplitudes (or \mathbf{r}_2 in EOM-CC), which means that we pick out a unique element $|ij^{ab}\rangle$, where $a > b$ and $i > j$, we generate the permutations and antisymmetrize them. During Davidson iterations, we also ensure that the trial vectors remain antisymmetric during the Gram-Schmidt orthonormalization process, as we found that if explicit antisymmetrization is not carried out, numerical noise may lead to the loss of the antisymmetry in new vectors during iterations.

With respect to the choice of starting vectors, differently from the eigenvalue case in which the pivoting was done on the basis of the value of the diagonal of $\bar{\mathbf{H}}$ (see Shee et al.⁸² for details), for linear systems, the pivoting is done on the basis of the magnitude of the property gradient ξ^X vector elements (from highest to lowest), in order to avoid selecting initial vectors with zero norm.

4. COMPUTATIONAL DETAILS

All coupled cluster linear-response calculations were carried out with a development version of the DIRAC code,^{48,92} employing the uncontracted singly augmented valence double- ζ Dyall basis set s-aug-dyall.v2z for the heavy elements (Zn,⁹³ Cd,⁹³ Hg,⁹³ Cs,⁹³ I,^{94,95} and Te^{94,95}), and a similar uncontracted Dunning basis set aug-cc-pVDZ for the light elements (H,⁹⁶ Li,⁹⁷ Na,⁹⁷ K,⁹⁸ F,⁹⁶ Cl,⁹⁹ O,⁹⁶ S,⁹⁹ Se,¹⁰⁰ and Br¹⁰⁰). In most calculations, we utilized the exact two-component (X2C)¹⁰¹ relativistic Hamiltonian, where the spin–orbit operator takes the form of an effective one-electron operator. The screening of the nuclear charges is in the version that we used approximated by an atomic mean field.¹⁰² To show the effect of relativity explicitly, we also provide results using the nonrelativistic Hamiltonian.^{103,104} We furthermore show some results with the spin-free X2C Hamiltonian in which spin–orbit coupling (SOC) terms are identified by transforming to the modified Dirac representation¹⁰⁵ and eliminated prior to defining the X2C transformation and Hamiltonian. To study the effect of electron correlation, we performed linear-response calculations based on mean-field methods like HF¹⁰⁶ as well as density-functional theory¹⁰⁷ (especially with the B3LYP¹⁰⁸ density functional approximation). The relativistic and nonrelativistic calculations have been carried out with the Gaussian type¹⁰⁹ and point charge nucleus model, respectively.

In our calculations, we have profited from the components of an ongoing implementation in ExaCorr of the Cholesky-decomposition^{110–112} approach to reduce the memory footprint of our calculations in the step to transform two-electron integrals from AO to MO basis by avoiding the storage in memory of the whole AO basis two-electron integral tensor. The Cholesky vectors (generated with a conservative threshold of 1×10^{-9} so as to retain most of them) are then used to explicitly form all six two-electron integral classes needed by the coupled cluster method. In a subsequent publication¹¹³ we shall address the use

of Cholesky vectors directly in the coupled cluster implementation of ground and excited state properties.

The molecular structures employed in all calculations are taken from the literature: in case of the diatomic molecules, from Huber and Herzberg¹¹⁴ for HX (X = F, Cl, Br, and I), I₂, ICl, from Hessel¹¹⁵ for NaLi, and from Ferber et al.¹¹⁶ for CsK. The internuclear distances employed are thus H–F (0.91680 Å), H–Cl (1.27455 Å), H–Br (1.41443 Å), H–I (1.60916 Å), Cl–I (2.32087 Å), I–I (2.6663 Å), Li–Na (2.81 Å), and K–Cs (4.285 Å). For the chiral molecules H₂Y₂ (Y = O, S, Se, and Te), the Y–Y bond length, H–Y bond length, and H–Y–Y bond angle are taken from Table 1 of Laerdahl and Schwerdtfeger,¹¹⁷ and the dihedral angle is kept fixed at 45 deg.

The size of the correlated virtual spinor spaces in the coupled cluster calculations is truncated by discarding spinors with energies above 5 au. For the IIB atoms, we correlate both semicore and valence electrons for Zn(3d,4s), Cd(4d,5s), and Hg(5d,6s). In the polarizability and optical rotation calculations of molecular systems, we correlate only the valence electrons. In the spin–spin coupling calculations, which are known to be more sensitive to core relaxation and correlation, we correlate all occupied and virtual orbitals.

All optical rotation calculations (HF, DFT, and CC) employed a common gauge origin, set to the origin of the coordinate system, chosen at the midpoint of the bond between the two chalcogen atoms, which nearly coincides with the system's center of mass. The atomic coordinates for each system under consideration as well as further details on the calculations (position of the center of mass, etc.) are provided respectively as XYZ and output files in the data set associated with this manuscript (see “Data Availability Statement”).

5. SAMPLE APPLICATIONS

5.1. Polarizability of IIB Atoms. We begin the discussion by analyzing the obtained results for the polarizability of the Zn, Cd, and Hg atoms and present in Table 2 the static polarizability

Table 2. Static Polarizability (au) of IIB Atoms Calculated with the X2C Hamiltonian

	Zn	Cd	Hg
NR–HF ^a	53.88	76.01	81.05
SF–HF ^b	50.58	63.65	44.90
HF	50.57	63.64	44.82
SF–CCSD ^b	40.42	48.28	35.35
CCSD	40.42	48.25	35.25
CCSD(T)	38.86	47.64	34.62
CCSD(T) (all virtual dz)	38.80	47.69	34.66
CCSD(T) (tz)	38.86	46.64	34.27
Exp	38.8 ± 0.80 ¹¹⁸	47.5 ± 2 ¹¹⁹	33.91 ± 0.34 ¹²⁰

^aNonrelativistic calculation with the Levy–Leblond Hamiltonian.

^bScalar relativistic calculation with the spin-free¹⁰⁵ X2C Hamiltonian.

of these atoms calculated by different methods. A comparison of the first three rows of this Table shows the growing influence of relativity on the static polarizability from Zn to Hg. For example, the relativistic HF value for Hg (44.82 au) is nearly half of its nonrelativistic counterpart (81.05 au). This is mainly due to the strong relativistic contraction of the 6s-shell.

In contrast, the effect of electron correlation at the CCSD level is rather constant for these elements (−10.15 au for Zn, −15.39 au for Cd, and −9.57 au for Hg).

For Zn, electron correlation primarily accounts for the discrepancy between HF and experimental results. However, for Cd and especially Hg, the inclusion of relativity is crucial. The above-mentioned contraction of the valence s-shell reduces the magnitude of the polarizability, whereas SOC becomes increasingly important by enabling spin-forbidden transitions. We will discuss this consequence of relativity in greater depth when looking at the frequency-dependence of polarizability in the next section.

An error of approximately 1–2 au remains between our relativistic CCSD results and the experimental values. To locate the source of this error, we performed CCSD(T) calculations using the finite-field method since the analytic gradient is not yet available for CCSD(T) in DIRAC. In these CCSD(T) finite-field calculations, we used an external electric strength of 0.005 au, which is sufficiently large to avoid numerical issues and small enough to remain in the linear regime.

From a comparison between the results of CCSD and CCSD(T), it is evident that the inclusion of the triple excitations indeed enhances the accuracy: from 95.99 to 99.84% for Zn, from 98.44 to 99.71% for Cd, and from 96.20 to 97.95% for Hg, respectively. In the results of CCSD(T), we also performed a calculation in which all virtual orbitals were used (so without energy truncation), but this did not significantly affect the results. Upon using the valence triple- ζ basis set s-aug-dyall.v3z, the Hg results improve and come close to the experimental error bar.

We now turn to the frequency-dependence of polarizability and look at the effect of SOC. In Figure 1, the frequency range from 0.0 to 0.30 au is displayed. The singularities at the frequencies of the spin-allowed transition $^1S_0 \rightarrow ^1P_1$ ($ns \rightarrow np$) dominate these curves, while the nonrelativistically spin-forbidden transition to the 3P state is clearly visible for Hg and, after zooming in on the transition energy, also already for Zn. Calculating and plotting the polarizability⁶⁰

$$\alpha_{\alpha\beta}(\omega) = - \sum_n \left[\frac{\langle 0 | \hat{\mu}_\alpha | n \rangle \langle n | \hat{\mu}_\beta | 0 \rangle}{E_n - \omega} + \frac{\langle 0 | \hat{\mu}_\beta | n \rangle \langle n | \hat{\mu}_\alpha | 0 \rangle}{E_n + \omega} \right] \quad (23)$$

over a range of frequencies, $\{\omega\}$, implicitly shows all excitation energies E_n in the associated energy range. However, when interested in the values of these energies, it is, of course, more efficient to directly solve for the poles by diagonalizing \mathbf{H} . To check the correctness of the implemented solvers, we therefore compared the linear response and EOM-EE results employing the same Hamiltonian and basis set. The resulting excitation energies are depicted in Figure 1 with red lines and do indeed precisely align with the pole locations in the polarizability curves.

Looking at the low-lying parity-allowed ($ns \rightarrow mp$) transitions in the studied frequency range, for Zn and Cd, we find two $ns \rightarrow (n)p$ transitions (A and B, respectively, spin-forbidden $^1S_0 \rightarrow ^3P_1^\circ$ and spin-allowed $^1S_0 \rightarrow ^1P_1^\circ$ transitions) and two $ns \rightarrow (n+1)p$ transitions (C and D, respectively, spin-forbidden and spin-allowed transitions). For Hg, on the other hand, only A and B are within the studied frequency range, with C and D coming at higher energies and therefore not observed.

On the right side of Figure 1, we also show a simulated spectrum of the first spin-allowed transition $^1S_0 \rightarrow ^1P_1^\circ$ by calculating the damped linear response function for both CC–CC and CC–CI models. While CC–CI is an approximation of the CC–CC model, we note that the CC–CI curve exhibits a shape very similar to that of CC–CC curves in that both are

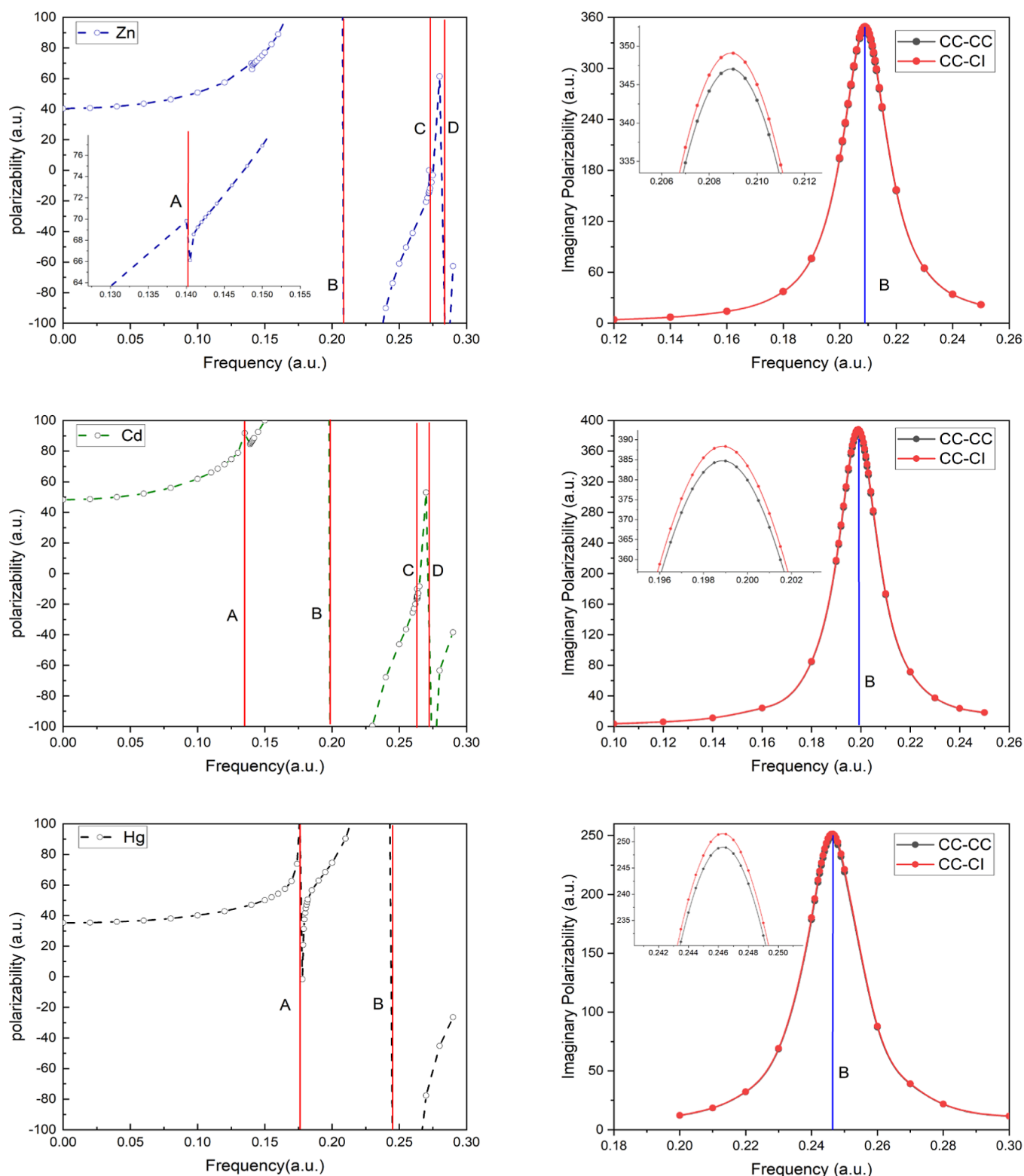


Figure 1. Frequency-dependent polarizability of Zn (top), Cd (middle), and Hg (bottom). The left figures show the real (undamped) polarizability with a frequency ranging from 0.0 to 0.30 au. The right figures, with insets to zoom in on the peak maxima, show the simulated spectra focusing on the B transition and are obtained from the imaginary part of the complex (damped) polarizability with an imaginary component of the frequency $\gamma = 0.01$ au. The red vertical lines are the EOM excitation energy: for Zn: A($^3P_1^o(4s^14p^1)$)0.1403 au; B($^1P_1^o(4s^14p^1)$)0.2089 au; C($^3P_1^o(4s^15p^1)$)0.2723 au; D($^1P_1^o(4s^15p^1)$)0.2828 au. For Cd: A($^3P_1^o(5s^15p^1)$)0.1356 au; B($^1P_1^o(5s^15p^1)$)0.1989 au; C($^3P_1^o(5s^16p^1)$)0.2634 au; D($^1P_1^o(5s^16p^1)$)0.2728 au. For Hg: A($^3P_1^o(6s^16p^1)$)0.1771 au; B($^1P_1^o(6s^16p^1)$)0.2463 au.

Lorentzian-type line shapes and share the exact same peak location since they solve the same response equation, as demonstrated in eq 19. The CC–CI model spectrum shows

only a minor difference in the peak height, with a relative error of about 1%. To verify the implementation of complex polarizability, we pay particular attention to the peak value of the

spectrum of the B atomic transition. Around the pole of the transitions we are investigating, the stationary point in the curves should be well approximated by the norm of the transition dipole moment divided by γ

$$\begin{aligned} \text{Im}(\alpha_{\alpha\beta}(\omega)) &= \text{Im} \left(- \sum_n \left[\frac{\langle 0|\hat{\mu}_\alpha|n\rangle\langle n|\hat{\mu}_\beta|0\rangle}{E_n - \omega - i\gamma} \right. \right. \\ &\quad \left. \left. + \frac{\langle 0|\hat{\mu}_\beta|n\rangle\langle n|\hat{\mu}_\alpha|0\rangle}{E_n + \omega + i\gamma} \right] \right) \\ &\approx \text{Im} \left(\frac{\langle 0|\hat{\mu}_\alpha|n\rangle\langle n|\hat{\mu}_\beta|0\rangle}{i\gamma} \right) \end{aligned} \quad (24)$$

In the current work, we set the imaginary component of the frequency γ as 0.01 au for all three atoms. Even though the EOM-CC transition dipole moment is not yet available in DIRAC, we can still compare the intensity ratios (Zn/Cd/Hg) between our results (1.39:1.55:1.0) and the values derived from the experimental lifetimes^{121–123} (1.48:1.54:1.0). It is noteworthy that our results qualitatively mirror the experimental trend. The small difference in ratios likely stems from the omission of a higher-order correlation and the quality of the basis set used. In [Supporting Information](#), we simulate the spectrum of BH molecules with damped CC–CC and find our results exactly reproduce the DALTON results.

To illustrate the effect of GPU acceleration in production calculations, we provide in [Table 3](#) an assessment of the

Table 3. Walltimes (in seconds) for the Aggregate Time for the Determination of the xx , yy , and zz Components of the Dipole Polarizability (LR) for the Hg Atom for GPU and CPU Execution, as a Function of Problem Size (Number of Occupied O and Virtual V Spinors)^a

O	V	time (s)		
		CPU	GPU	speedup
12	102	773	317	2.4
18	148	5485	1524	3.6
18	180	10,879	2606	4.2

^aAll calculations employed 1 OpenMP thread.

difference in performance between CPU and GPU-based execution for the determination of the response functions for Hg atoms, with the same correlation orbital space and basis set used above (12 occupied and 102 virtual spinors), as well as for slightly larger spaces.

Our results indicate that the speedup increases as the problem size increases, but even for relatively small problem sizes, GPU offloading remains advantageous in practice as a means to speed up our calculations. In the [Supporting Information](#), we provide details on the node architecture as well as additional discussion on speedups for the evaluation of the EOM-EE sigma vector.

5.2. Polarizability of Molecules. As our implementation is mainly intended for molecular systems, we will now look at results for molecular polarizabilities, which may have up to three distinct values upon diagonalizing the polarizability tensor. For diatomic and other symmetric molecules, it is sufficient to consider the mean dipole polarizability $\alpha(\omega)$ and the anisotropy $\Delta\alpha(\omega)$

$$\alpha(\omega) = \frac{1}{3}(\alpha_{zz}(\omega) + \alpha_{xx}(\omega) + \alpha_{yy}(\omega)) \quad (25)$$

$$\Delta\alpha(\omega) = \alpha_{zz}(\omega) - \frac{1}{2}(\alpha_{xx}(\omega) + \alpha_{yy}(\omega)) \quad (26)$$

where z is the molecular symmetry axis. In [Table 4](#), we list the static mean and anisotropic polarizability of hydrogen halides and alkali-metal diatomic molecules assessed by HF, B3LYP, and CC models with both relativistic (X2C) and nonrelativistic Hamiltonians and the corresponding experimental values as well. Unless otherwise specified, “CC” refers to “CC–CC–LR”.

The HF results deviate from the experimental value for both the mean and anisotropic polarizability, and the impact of the relativistic effect increases as we move from lighter to heavier molecules. For example, the relativistic correction is nearly zero for hydrogen fluoride but amounts to 1.3 au for I₂. In the case of the CsK molecule, the relativistic correction at the HF level is 31 au, emphasizing the necessity of considering the relativistic effect in the calculation of heavy elements. For this molecule, the effect of relativity may again be rationalized in terms of contraction of the outermost valence s-orbitals, in particular that of Cs, which reduces the polarizability, similar to what we observed in the Hg atom.

Apart from relativity, another source of discrepancy between HF and experiment lies in the importance of the electron correlation. Electron correlation is modeled in DFT by the B3LYP functional and explicitly calculated in the CC models. From the results, it is evident that in both cases, the electron correlation and the relativistic correction are not strictly additive. For example, when computed with CC, the relativistic corrections for I₂ and CsK are 0.91 au and –26 au, respectively, while they are 1.30 au and –31 au when computed with HF.

The B3LYP calculations yield much better values than HF for both the relativistic and nonrelativistic Hamiltonian. The relativistic correction on the B3LYP model is similar in magnitude to that found for HF but with a different sign. For instance, the relativistic correction of anisotropic polarizability for CsK for HF is +9 au, while it is –11 au in B3LYP. For the halides, the B3LYP calculations yield values that are close to the CC results and are within or only slightly outside the experimental error bars for both isotropic and anisotropic polarizability. However, for the alkali-metal diatomic molecules NaLi and CsK, the B3LYP values significantly deviate from the experimental value.

The CC results are close to the experimental data for both halide and alkali-metal molecules. We have also tried using the triple- ζ basis set for CC on three light hydrogen halide molecules (HF, HCl, and HBr) to reduce the error and indeed observe an improvement of CC values, which then fall within the experiment error bar for the isotropic polarizability. Getting the smaller anisotropic polarizability to agree with experimental data is more demanding on the model and may require the addition of more diffuse functions and/or the inclusion of triple excitations.

One may note for the anisotropic polarizability of HI the considerable deviation of all three theoretical values (around 2 au) from the experimental value of 11.4 au that was determined in 1940 by Denbigh.¹²⁴ Curiously, this value appears to have not been re-evaluated since then, while the isotropic polarizabilities of HCl and HBr, which were also reported by Denbigh, were later estimated to be significantly lower by Kumar and Meath.¹²⁵ The anisotropy of HBr that was given as 6.14 au by Denbigh was adjusted to just 1.7 au by Pinkham and Jones,¹²⁶ but we could

Table 4. Static Dipole Polarizability (au) of Diatomic Molecules

	HF ^a	HF ^b	B3LYP ^a	B3LYP ^b	B3LYP ^c	CC ^a	CC ^b	CC ^c	exp
Mean Dipole Polarizability									
HF	4.40	4.40	5.11	5.12	5.57	5.04	5.05	5.52	5.60 ± 0.10 ¹²⁵
HCl	15.51	15.54	16.34	16.38	17.53	16.06	16.09	17.14	17.39 ± 0.20 ¹²⁵
HBr	21.86	21.90	22.85	22.94	24.43	22.52	22.58	24.02	23.74 ± 0.50 ¹²⁵
HI	33.62	33.50	34.63	34.69	36.71	34.36	34.30		35.30 ± 0.50 ¹³¹
ICl	46.48	46.52	47.53	47.66	49.80	47.48	47.59		43.8 ± 4.4 ¹³²
I ₂	67.90	69.20	68.72	69.92	72.55	68.81	69.72		69.7 ± 1.8 ¹³³
NaLi	231	230	210	209	210	240	240	239	263 ± 20 ¹³⁴
CsK	723	692	581	548	549	637 ^d	611 ^d		601 ± 44 ¹³⁵
Anisotropic Dipole Polarizability									
HF	1.79	1.79	1.91	1.91	1.46	1.96	1.96	1.45	1.62 ¹³⁶
HCl	2.35	2.34	2.18	2.16	1.66	2.39	2.38	1.85	2.10 ¹³⁷
HBr	2.43	2.45	1.98	1.92	1.65	2.35	2.30	2.02	1.7 ¹²⁶
HI	2.66	2.81	2.09	2.00	1.87	2.60	2.51		11.4 ¹²⁴
ICl	26.14	26.96	24.27	24.63	24.50	25.30	25.82		
I ₂	44.92	49.01	41.31	43.75	42.88	44.00	45.87		45.1 ± 2.3 ¹³³
NaLi	92	92	109	109	108	154	154	149	
CsK	353	362	400	389	390	510 ^d	499 ^d		

^aNonrelativistic calculation using the Levy-Leblond Hamiltonian. ^bRelativistic calculation using the X2C Hamiltonian. ^cUsing the diffuse Triple- ζ basis set. ^dCorrelate both 6s and 5p electrons of Cs.

not find a similar re-evaluation of the anisotropic polarizability of HI on the basis of experimental data in the literature. This discrepancy between theory and the old experimental value for anisotropy was also noted in the theoretical work of Maroulis¹²⁷ and Iliáš et al.¹²⁸ Iliáš et al. used relativistic CCSD(T) and included vibrational corrections on both dipole moment and static polarizability and found their results to be significantly lower than the experimental value: their anisotropic polarizability was 2.33 ± 0.05 au, which agrees well with the current relativistic CC linear response value of 2.51 au. While their suggestion that also the experimental value^{129,130} of the dipole moment could be inaccurate could not be sustained,^{129,130} we agree that the discrepancy between theory and experiment for the anisotropic polarizability is likely due to an inaccuracy in the experimental value. Nonetheless, it would be nice to put more firm error bars on the theoretical value as well by employing a larger basis set, including the g and h functions. This was not feasible with our current implementation due to memory constraints related to the use of a single compute node.

We now turn our attention to the frequency-dependent polarizability and focus on the I₂ molecule, given the extensive experimental research on this molecule and the abundance of experimental spectral data that can be used to validate theoretical models. Relevant in the frequency region that we consider are the lowest electronically excited states that arise from the $\sigma_g^2\pi_u^4\pi_g^3\sigma_u^1$ and $\sigma_g^1\pi_u^4\pi_g^4\sigma_u^1$ configurations. These are primarily triplet states that are denoted in the literature¹³⁸ as $A^3\Pi_u$, $B^3\Pi_u$ and $C^3\Sigma_u$, with the latter originating from the second configuration. The lowest singlet state arises from the first configuration and is indicated as $^1B''$. In Table 5, we present the computed frequency-dependent polarizability for three theoretical methods alongside the experimental values¹³³ measured by Maroulis et al. at three frequencies. Like the experimental values, the values computed with CC at these three frequencies are quite close to each other, and we find reasonable agreement with the CC values slightly underestimating the experimental data. The HF and B3LYP results deviate rather strongly from the experimental results for the first two frequencies, which can be rationalized as being caused by an error in the position of the

Table 5. Frequency Dependent Polarizability (au) of the I₂ Molecule

	$\alpha_{zz}(\omega)$	$\alpha_{xx}(\omega)$	$\alpha(\omega)$
$\omega_1 = 15,798 \text{ cm}^{-1}$			
HF	152.0	55.0	87.4
B3LYP	-10.7	58.7	35.6
CC	114.8	55.8	75.5
exp ¹³³			86.8 ± 2.2
$\omega_1 = 16,832.3 \text{ cm}^{-1}$			
HF	-97.3	56.0	4.9
B3LYP	75.4	62.0	66.5
CC	124.0	56.8	79.2
exp ¹³³			93.6 ± 3.4
$\omega_1 = 30,756.9 \text{ cm}^{-1}$			
HF	117.9	55.3	76.2
B3LYP	114.5	61.0	78.8
CC	113.9	59.9	77.9
exp ¹³³			95.3 ± 1.9

pole close to the first two laser frequencies, which is computed at too low an energy with HF and DFT (B3LYP). Due to the selection rules for this transition to the $B^3\Pi_{(0^+u)}$ state, this then leads to a negative value of the parallel (zz-)component of the polarizability for HF and B3LYP, while the perpendicular (xx-)component is not affected and has a similar value for HF, B3LYP, and CC.

Rather than looking at the values for just these three frequencies, two of which are close to the X → B transition, it is more illustrative to apply eq 22 and plot simulated absorption cross-section curves. We scan the wavelength ranging from 400 to 700 nm and set the imaginary component of the complex frequency (γ) to 0.005 au, which corresponds to the experimental lifetime of the $B^3\Pi_0^+$ state. As selection rules are different for the transitions to the $B^3\Pi_0^+$ and $C^1\Pi_1$ states, we may thereby identify the zz-component of the complex dipole electric polarizability as being (primarily) due to the $B^3\Pi_0^+$ state, while the xx-component is due to the $C^1\Pi_1$ state. This facilitates the comparison to the experimental analysis that was carried out

by Tellinghuisen.¹³⁹ The resulting curves for three models, NR–HF (green lines), X2C–HF (red lines), and X2C–CC (blue lines), are depicted in Figure 2 and clearly show the effect of

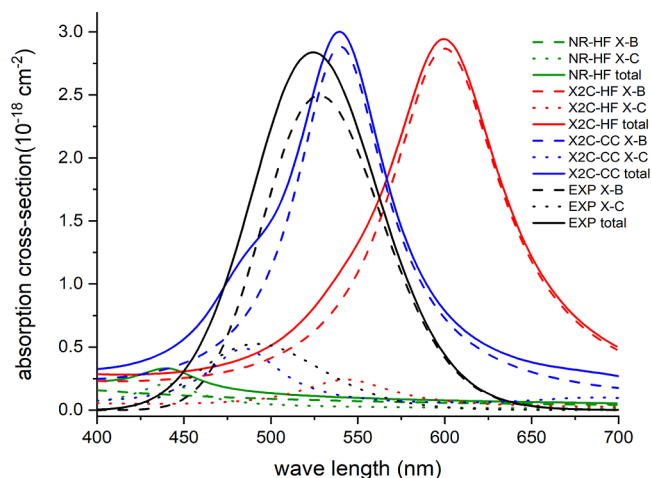


Figure 2. Simulated spectrum of I_2 . The green lines are nonrelativistic HF, the red lines are X2C–HF, the blue lines are X2C–CC, and the black lines are experimental values from the work of Tellinghuisen.¹³⁹ The dashed lines represent the contribution of the transition from the ground state $X^1\Sigma_0^+$ to the $B^3\Pi_0^+$ state. The dot lines are contributions of transition from the $X^1\Sigma_0^+$ state to the $C^1\Pi_1$ state. The solid lines are the total absorption cross-section.

SOC. The NR computed curves are entirely due to the weaker transition from $X^1\Sigma_0^+$ to $C^1\Pi_1$ and severely underestimate the absorption cross-section. With SOC, this transition becomes a shoulder on the dominant $X^1\Sigma_0^+$ to $B^3\Pi_0^+$ transition. Comparison with the measured curves (black lines) from the work of Tellinghuisen¹³⁹ shows quite good agreement for the height of the dominant peak that is slightly red-shifted compared to the experimental transition.

The dominant peak in the X2C–HF exhibits a severe red shift, which clarifies the error seen in the frequency-dependent polarizability in Table 5. For the peak values, the X2C–HF result of $2.95 \times 10^{-18} \text{ cm}^{-2}$ is, however, quite close to the X2C–CC value of $2.98 \times 10^{-18} \text{ cm}^{-2}$, suggesting that the value of the transition dipole moment is similar in both models under the current calculation conditions. This suggests that the relativistic HF model does describe this excited state qualitatively well, albeit at the wrong energy.

Regarding the spin-allowed transition from $X^1\Sigma_0^+$ to the $C^1\Pi_1$ state, displayed by the dotted line in Figure 2, we observe the X2C–CC model to agree well with the experimental analysis of Tellinghuisen.¹³⁹ The discrepancy in pole location is around 20 nm, and the difference in the peak value is minor at $0.02 \times 10^{-18} \text{ cm}^{-2}$.

To further analyze the results, we calculate and present the excitation energies of the $B^3\Pi_0^+$ and $C^1\Pi_1$ states in Table 6. We note that HF underestimates the excitation energy of $B^3\Pi_0^+$ compared to the CC values, no matter what relativistic effects

are included. This can be attributed to the triplet instability of the TDHF model.^{140–148} On the other hand, such underestimation can be largely avoided by using the simpler configuration interaction singles (CIS) approach. Thus, we perform nonrelativistic CIS calculations by DALTON and find that the CIS value indeed is higher by about 0.011 au for the $B^3\Pi_0^+$ state.

For singlet state $C^1\Pi_1$, HF excitation energies are larger than the CC values in both nonrelativistic and spin-free calculations. However, when SOC is introduced via X2C, HF energies become lower. While SOC raises the excitation energy in CC, it reduces the excitation energy in HF, implying that SOC effects and correlation are again not additive.

In the Supporting Information, we provide a calculation of the spectrum of the BH molecule, which was used to verify the correctness of our implementation. We compare our damped CC-LR calculation with the broadening of the coupled cluster transition dipole moment computed by the DALTON program^{39,149} and find good agreement.

5.3. Spin–Spin Coupling. In the previous section, we investigated electric properties. In the current section, we show a calculation of the indirect nuclear spin–spin coupling constant as an illustrative example of the use of our implementation for a magnetic property. The coupling constant K_{KL} can be related to the experimentally observed coupling J_{KL} between the nuclear spins of atoms K and L via

$$J_{KL} = \frac{1}{2\pi} \gamma_K \gamma_L K_{KL} \quad (27)$$

where γ_K is the gyromagnetic ratio of nucleus K. The K_{KL} tensor can, in a relativistic framework, be expressed in terms of linear response functions with respect to the hyperfine operator \hat{h}_K^{hfs}

$$K_{KL,\mu\nu} = \frac{\partial^2}{\partial m_{K,\mu} \partial m_{L,\nu}} \langle \langle \hat{h}_K^{\text{hfs}} ; \hat{h}_L^{\text{hfs}} \rangle \rangle \quad (28)$$

$$\hat{h}_K^{\text{hfs}} = \frac{1}{c} \sum_i \mathbf{m}_K \cdot \frac{\mathbf{r}_{iK} \times \boldsymbol{\alpha}}{r_{iK}^3} \quad (29)$$

In the nonrelativistic framework, it is common to formulate K_{KL} in terms of three distinct contributions: diamagnetic spin–orbit coupling (DSO), paramagnetic spin–orbit (PSO), and the Fermi contact-spin dipolar (FC-SD) term. Of these, the first term can be computed as an expectation value, whereas the second and third require the use of response theory. Moreover, the PSO term involves only singlet excitations, whereas the FC-SD term couples a singlet ground state to triplet excited states due to the triplet nature of the Fermi contact and spin-dipolar operators. An explicit sum-over-states form of the contributions to K_{KL} in the nonrelativistic framework is^{9,150}

Table 6. Excitation Energy (au) for I_2

states	NR–HF	NR–CIS ^a	NR–CC	SF–HF	SF–CC	X2C–HF	X2C–CC
$B^3\Pi_0^+$	0.065	0.076	0.076	0.060	0.070	0.076	0.084
$C^1\Pi_1$	0.103	0.107	0.098	0.097	0.092	0.084	0.094

^aCalculations were performed using the DALTON program.

$$K_{\text{KL}} = \frac{1}{2c^4} \left\langle 0 \left| \frac{\mathbf{r}_K^T \mathbf{r}_L^T I - \mathbf{r}_K \mathbf{r}_L^T}{r_K^3 r_L^3} \right| 0 \right\rangle - \frac{2}{c^4} \sum_{n_S} \frac{\langle 0 | r_K^{-3} I_K | n_S \rangle \langle n_S | r_L^{-3} I_L | 0 \rangle}{E_{n_S} - E_0} - \frac{2}{c^4} \sum_{n_T} \frac{\langle 0 | \frac{8\pi}{3} \delta(r_L) \mathbf{s} + \frac{3r_L r_L^T - r_L^2 I_L}{r_L^5} \mathbf{s} | n_T \rangle \langle n_T | \frac{8\pi}{3} \delta(r_L) \mathbf{s}^T + \frac{3r_L r_L^T - r_L^2 I_L}{r_L^5} \mathbf{s}^T | 0 \rangle}{E_{n_T} - E_0} \quad (30)$$

As discussed in ref 151, the PSO and FC-SD response functions can, in the relativistic framework of eq 28, be identified as orbital responses involving rotations among positive energy orbitals. The DSO contribution, on the other hand, comes from the rotations between positive and negative energy orbitals and can, in a sequence of approximations, be brought into an expectation value form that is identical to the nonrelativistic expression and is then called the Sternheim approximation.¹⁵² Therefore, in relativistic calculations, there are two ways to obtain the diamagnetic terms: one by including electron-positron rotations explicitly in the response calculation or by making use of the Sternheim approximation.

In contrast to the Sternheim approximation, in which a numerically very stable expectation value is computed, the formally more rigorous response approach is quite sensitive to the quality of sampling of the positronic orbital space on a finite basis.^{64,151} This is why, in the current study, we compute the diamagnetic terms as an expectation value. An important modification as compared to the original application in 4-component theory is the use of the X2C transformation, in which all operators are first transformed to a 2C representation. The generic expression is

$$\mathbf{X}^{\text{X2C}} = \mathbf{X}^{++} = \sum_{V,W}^{L,S} [\mathbf{U}^{V+}]^\dagger \mathbf{X}^{\text{VW}} \mathbf{U}^{W+} \quad (31)$$

in which \mathbf{U}^{L+} and \mathbf{U}^{S+} are blocks of the X2C transformation matrix that block-diagonalizes the matrix representation of a reference Hamiltonian operator (usually and also in this work taken as the molecular Hamiltonian without two-electron interactions) and allows to solve only for positive (+) energy solutions. In the case of magnetic properties, the original 4C matrix representation of operator (29) is off-diagonal with respect to the large (L) and (S) small parts of the 4C basis so that

$$\mathbf{h}_K^{\text{hfs,X2C}} = \frac{1}{c} [\mathbf{U}^{L+}]^\dagger \left[\mathbf{m}_K \cdot \frac{\boldsymbol{\sigma} \times \mathbf{r}_{iK}}{r_{iK}^3} \right]^{LS} \mathbf{U}^{S+} + \text{h.c.} \quad (32)$$

This matrix representation can be interpreted as providing the X2C equivalent of the singlet PSO and triplet FC-SD operators that are used in nonrelativistic response calculations. The Sternheim approximation yields a diagonal 4C DSO operator \mathbf{k}_{KL} that is transformed as

$$\mathbf{k}_{\text{KL}}^{\text{X2C}} = [\mathbf{U}^{L+}]^\dagger \mathbf{k}_{\text{KL}}^{\text{LL}} \mathbf{U}^{L+} + [\mathbf{U}^{S+}]^\dagger \mathbf{k}_{\text{KL}}^{\text{SS}} \mathbf{U}^{S+} \quad (33)$$

$$\mathbf{k}_{\text{KL}}^{\text{VW}} = \frac{1}{2c^4} \left[\frac{\mathbf{r}_K^T \mathbf{r}_L^T I - \mathbf{r}_K \mathbf{r}_L^T}{r_K^3 r_L^3} \right]^{\text{VW}} \delta_{\text{VW}} \quad (34)$$

and contracted with the unperturbed density matrix to obtain the DSO contribution to the spin–spin coupling.

In Table 7, we list the resulting reduced isotropic and anisotropic spin–spin coupling constants of HX (X = F, Cl, Br, and I) computed by HF, B3LYP, CC–CI, and CC–CC models with both nonrelativistic and relativistic Hamiltonians. As is well known, relativistic effects are very important for magnetic

Table 7. Isotropic and Anisotropic Reduced Spin–Spin Coupling K ($10^{19} \text{ m}^{-2} \text{ kg s}^{-2} \text{ A}^{-2}$) for HX (X = F, Cl, Br, and I)

models	$^1\text{H}^{19}\text{F}$	$^1\text{H}^{35}\text{Cl}$	$^1\text{H}^{79}\text{Br}$	$^1\text{H}^{127}\text{I}$
Isotropic				
NR–HF	49.5486	28.1528	10.8253	−0.8979
NR–B3LYP	33.3898	19.7146	−1.8769	
NR–CC–CI	40.5554	31.3181	30.7926	
NR–CC–CC	40.4794	31.0971	29.9730	
NR–CC–CC ^a	40.4778	31.0970	29.9729	
X2C–HF	49.5023	27.2261	−4.5338	−83.1522
X2C–B3LYP	33.2367	18.9409	−11.6914	−57.3316
X2C–CC–CI	40.4834	30.9008	23.8246	3.4887
X2C–CC–CC	40.4047	30.6448	22.7588	0.7481
DC–HF	49.4725	27.1494	−4.8396	−84.0079
Anisotropic				
NR–HF	2.5499	59.6666	161.9806	277.7237
NR–B3LYP	6.3484	50.1075	130.4249	
NR–CC–CI	−3.7566	36.3828	100.9785	
NR–CC–CC	−3.4931	37.1193	102.9362	
X2C–HF	2.5858	60.2375	168.5425	305.7204
X2C–B3LYP	6.4477	50.3990	130.5655	201.0597
X2C–CC–CI	−3.6579	36.8838	106.6559	192.8454
X2C–CC–CC	−3.3929	37.6281	108.7226	196.3474
DC–HF	2.5978	60.2822	168.7214	306.1280

^aCalculations were performed using the CFOUR program.

properties, and we see the expected increase of their magnitude upon descending the periodic table from hydrogen fluoride to hydrogen iodide. To benchmark the quality of the X2C transformation, we also carried out four-component DC HF calculations with a default approximation for all small two-electron integrals,¹⁵³ and we saw that the X2C values match the DC results very well for all molecules.

At the HF level, the isotropic constants generally exhibit a downward trend from HF to HI, while the anisotropic values typically show an upward trend for both relativistic and nonrelativistic calculations. After including electron correlation, these trends are qualitatively the same, although the precise values change considerably, especially for HBr. To verify our CC implementation, we also utilize the CFOUR program¹⁵⁴ for nonrelativistic CC response and find our CC–CC models with the nonrelativistic Hamiltonian to reproduce the CFOUR values for all three light molecules.

Although the nonrelativistic calculation is useful for analysis, we cannot ignore the relativistic effects of heavy molecules. For example, the relativistic correction at the coupled cluster level for HBr is around 25% and slightly smaller than that with HF. We also performed DFT calculations; the results obtained with B3LYP functionals are quite far from both the HF and the CC results. As there are no suitable experimental values to compare with, one cannot assess rigorously the performance of the methods, but the large discrepancy between the commonly used B3LYP DFT and CC makes these systems of interest for future benchmarking with converged CC expansion (we deem both our employed basis set as well as excitation level not yet suitable for this purpose).

Looking at the two ways of carrying out CC response calculations, we observe minor variances between CC–CI and CC–CC, which appear to become more pronounced for the heavier elements. It is known that LR–CC transition moments are size-extensive whereas EOM–CC ones are not;^{41,46,155–161} though in these comparisons, it was found that the numerical

differences between LR-CC and EOM-CC were rather small for a single molecule. Numerical studies have been primarily concerned with light molecules and properties within the valence domain, like the electric transition dipole moment,^{46,159,161} and the dipole polarizability,^{155,158} and our results for polarizabilities are in line with these findings. A notable exception is the work of Sekino and Bartlett,¹⁵⁸ who have investigated spin–spin couplings for ethane and found a difference of 0.05% between EOM-CC and LR-CC for J_{CC} . This value is comparable to our difference of about 0.19% for the HF molecule.

If the lack of size extensivity in EOM-CC transition moments is a significant source of discrepancies, one would expect the difference between CC–CI and CC–CC to grow as the number of electrons correlated increases across the HX series but the difference per correlated electron to remain roughly constant. Our analysis of the zz , xx , and yy components of the linear response contribution to K_{HX} (see [Supporting Information](#)) provides some evidence this is the case, as differences (in absolute value) for each component fall between 0.004 and 0.02 au for all molecules. There are some differences between Hamiltonians for HBr and HI, but these are of smaller magnitude than those due to nonextensivity. However, we believe the sample size is not large enough for definitive conclusions, and in future investigations, we intend to revisit this issue for a broader range of molecules.

As most experimental work is carried out in the condensed phase, we wanted to go beyond isolated diatomic molecules and provide a sample investigation of solvent effects. For this purpose, we chose the solvent shift on the spin–spin coupling constant $^1\text{H}_b\text{-}^{34}\text{Se}$ in the $\text{H}_2\text{Se-H}_2\text{O}$ dimer. The supermolecular structure is taken from the work of Olejniczak et al.¹⁶² and displayed on [Figure 3](#). It can readily be seen from [Table 8](#) that all

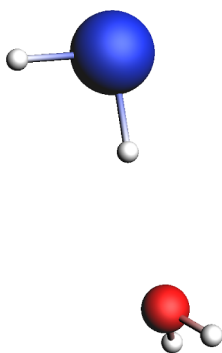


Figure 3. $\text{H}_2\text{Se-H}_2\text{O}$ complex system. Color of atoms: Se (blue), O (red), and H (white); H_b is the Hydrogen atom that belongs to Se and is close to O.

calculations show the solvent effect on the Se– H_b coupling for the hydrogen bond to be quite substantial. However, the shifts ΔJ in the correlated models have a magnitude different from that at the HF level. For example, the shifts of Se– H_b are 19.5403 and 19.0648 Hz for CC–CC and B3LYP, respectively, while they are almost twice as large at 40.0220 Hz for HF. Although the shifts of DFT are quite close to those computed with CC, the absolute $J_{\text{iso}}^{\text{super}}$ and J_{iso} deviate a lot. Comparing with BLYP and B3LYP values, we find the addition of exact exchange to the DFT to have a significant effect, with the hybrid DFT B3LYP results being closer to the CC values.

5.4. Optical Rotation. Finally, we consider both electric and magnetic fields by looking at optical rotation (in the length gauge and for a common gauge origin) for the archetypical chiral molecules H_2Y_2 ($\text{Y} = \text{O}, \text{S}, \text{Se}, \text{and Te}$). At the frequency of the sodium D-line (in 589.29 nm), which is the most common experimental setup, the specific optical rotation $[\alpha]_{\text{D}}^{25}$ in unit $[\text{deg dm}^{-1} (\text{g/mol})^{-1}]$ is given by the equations⁷⁴

$$[\alpha]_{\text{D}}^{25} = -228 \times 10^{-30} \frac{\pi^2 N a_0^4 \omega}{3M} \sum_{\alpha} G'_{\alpha\alpha} \quad (35)$$

$$G'_{\alpha\beta}(-\omega; \omega) = -\text{Im}\langle\langle \hat{\mu}_{\alpha}; \hat{m}_{\beta} \rangle\rangle_{\omega} \quad (36)$$

where M is the molecular mass in g mol^{-1} , N is the number density, and $\hat{\mu}_{\alpha}$ and \hat{m}_{β} are cartesian components of the electric and magnetic dipole operator, respectively.

In [Figure 4](#), we display the results for HF, B3LYP, and CC for both the nonrelativistic Hamiltonian and the X2C Hamiltonian. First, to verify our implementation, we performed the calculation on H_2S_2 with the DALTON program with the same basis set. The resulting data are available in the [Supporting Information](#) and show good agreement, confirming the correctness of the implementation. To benchmark the influence of the truncation on the virtual orbital space, we furthermore performed a calculation in which we truncated the virtual orbital space with an energy threshold of 100 au instead of the otherwise used value of 5 au and found that the results match up to 99%. This is similar to the tendency observed in the electric dipole polarizability, as expected, as both optical rotation and electric dipole polarizability are predominantly determined by the valence electrons and do not require core-like high-energy virtuals.

[Figure 4](#) shows that for the lighter molecules, H_2O_2 and H_2S_2 , the B3LYP and CC values are nearly twice as large than as of the HF. While the relativistic effect is negligible for H_2O_2 , with a correction of less than 1%, it cannot be neglected for H_2S_2 , where it rises to 10%. The impact of the relativistic effect is present for all models, but correlation and relativistic effects are again not additive. For instance, we find a relativistic HF correction of $-12 [\text{deg dm}^{-1} (\text{g/mol})^{-1}]$, while for B3LYP and CC, these corrections are -26 and $-18 [\text{deg dm}^{-1} (\text{g/mol})^{-1}]$, respectively. For the heavier molecules H_2Se_2 and H_2Te_2 , the values computed for the sodium D-line frequency become exceedingly large, as these molecules have an excitation that is almost at resonance with this frequency. To better understand this phenomenon, we have therefore calculated the excitation energy of the first 11 microstates for these two molecules. The resulting values are compiled and presented in [Table 9](#). Note that we display all degenerate components of triplet states for better comparison to relativistic states.

The computed excitation values show that in the case of H_2Se_2 , the relativistic CC value is significantly larger than the nonrelativistic CC because the employed frequency is quite close to the resonance frequency of the second excited state in the relativistic calculation (0.0789 au), whereas it is distant from all excited states in the nonrelativistic CC calculation. For the B3LYP computations, we see that the frequency is close to the fourth excited state in both relativistic and nonrelativistic scenarios (0.0863 and 0.0889, respectively). This proximity results in large values being obtained from both calculations.

When we examine the H_2Te_2 molecule, we find the relativistic effect to be substantial for all three models, even reversing the sign of the optical rotation. For example, the nonrelativistic CC

Table 8. Isotropic and Anisotropic Indirect Spin–Spin Coupling (J_{iso} and J_{aniso} in Hz) for Isolated H_2Se Subsystem, ($J_{\text{iso}}^{\text{super}}$ and $J_{\text{aniso}}^{\text{super}}$ in Hz) for H_2Se Subsystem in $\text{H}_2\text{Se}-\text{H}_2\text{O}$, and the Shifts (ΔJ , in Hz) for the Isolated (“ME”) H_2Se Molecules in the Presence of H_2O

models	J_{iso}	$J_{\text{iso}}^{\text{super}}$	$\Delta J_{\text{iso}}^{\text{ME}}$ $^1\text{H}_b\text{-}^{34}\text{Se}$	J_{aniso}	$J_{\text{aniso}}^{\text{super}}$	$\Delta J_{\text{aniso}}^{\text{ME}}$
HF ^a	90.4949	128.2837	36.7888	305.8746	302.1583	−3.7163
HF	52.7369	92.7589	40.0220	353.6191	353.4049	−0.2142
BLYP	−26.8400	−11.0675	15.7725	265.5061	271.8454	6.3393
B3LYP	−9.1404	9.9244	19.0648	269.7740	275.2143	5.4403
CC–CI	66.6432	85.8755	19.2303	215.4586	218.7408	3.2821
CC–CC	65.9553	85.4956	19.5403	219.8036	223.0023	3.1987

^aNonrelativistic calculation with the Levy-Leblond Hamiltonian.

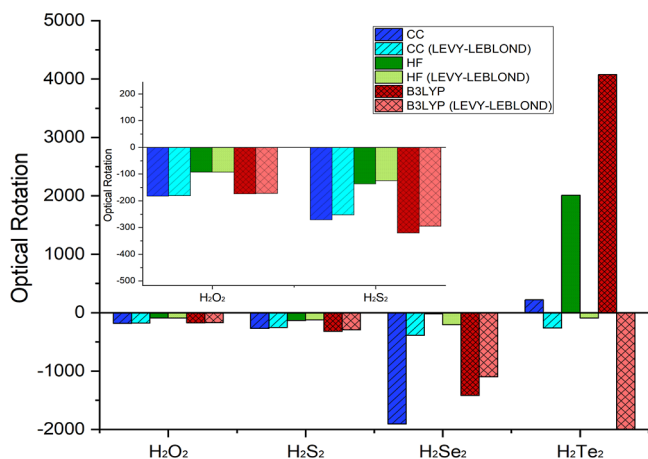


Figure 4. Optical rotation of hydrogen peroxide series (H_2Y_2) in $[\text{deg dm}^{-1} (\text{g/mol})^{-1}]$ with a frequency corresponding to the sodium D-line (589.29 nm, 0.077319 au) calculated with the X2C and Levy-Leblond Hamiltonians.

value is $-263.59 [\text{deg dm}^{-1} (\text{g/mol})^{-1}]$, but the relativistic CC is $218.83 [\text{deg dm}^{-1} (\text{g/mol})^{-1}]$. Besides reversing the sign, with HF also, the magnitude of the optical rotation is very different in the relativistic and nonrelativistic cases. This is because the first six excited states, while being close to transitions, are triplets and hence do not contribute to the optical rotation that is observed in the nonrelativistic case. In the relativistic case, SOC makes these transitions allowed, which, combined with their proximity to the sodium D-line, leads to a much larger optical rotation of the opposite sign than computed nonrelativistically. The B3LYP values are large in both the relativistic and the NR cases because the frequency is then close to the singlet state (0.0721 au and 0.0777 au, respectively). To avoid artifacts due to the proximity of poles and the associated infinity of the real frequency-dependent response function, it is probably opportune to consider the lifetime of the excited state and use damped response theory like shown for the complex polarizability of I_2 .

In addition, we observe triplet instability in the HF results as well, similar to what we observed for I_2 . For example, we note that the excitation energy of HF's first triplet is larger than that in CC. In HF calculations, the second triplet state lies below the

Table 9. Excitation Energy (au) of the First 11 Microstates for H_2Se_2 and H_2Te_2

	state	HF	HF ^a	B3LYP	B3LYP ^a	CC	CC ^b	CC ^a
H_2Se_2	1	0.0671	0.0719	0.0639	0.0661	0.0789	0.0785	0.0812
	2	0.0672	0.0719	0.0639	0.0661	0.0789	0.0785	0.0812
	3	0.0699	0.0719	0.0642	0.0661	0.0792	0.0788	0.0812
	4	0.0860	0.0954	0.0863	0.0889	0.0988	0.0984	0.1016
	5	0.0911	0.0954	0.1098	0.1121	0.1285	0.1282	0.1309
	6	0.0913	0.0954	0.1099	0.1121	0.1286	0.1282	0.1309
	7	0.1082	0.1083	0.1100	0.1121	0.1288	0.1284	0.1309
	8	0.1289	0.1315	0.1314	0.1343	0.1443	0.1440	0.1478
	9	0.1293	0.1315	0.1497	0.1510	0.1541	0.1541	0.1561
	10	0.1295	0.1315	0.1499	0.1510	0.1543	0.1542	0.1561
	11	0.1600	0.1624	0.1500	0.1510	0.1545	0.1544	0.1561
H_2Te_2	1	0.0517	0.0635	0.0542	0.0584	0.0672	0.0672	0.0721
	2	0.0517	0.0635	0.0543	0.0584	0.0673	0.0673	0.0721
	3	0.0605	0.0635	0.0558	0.0584	0.0689	0.0686	0.0721
	4	0.0697	0.0924	0.0721	0.0777	0.0835	0.0835	0.0898
	5	0.0873	0.0924	0.0931	0.0968	0.1098	0.1097	0.1143
	6	0.0888	0.0924	0.0935	0.0968	0.1101	0.1100	0.1143
	7	0.0993	0.0957	0.0940	0.0968	0.1109	0.1108	0.1143
	8	0.1098	0.1138	0.1102	0.1158	0.1220	0.1220	0.1292
	9	0.1123	0.1138	0.1316	0.1320	0.1349	0.1349	0.1367
	10	0.1139	0.1138	0.1324	0.1320	0.1357	0.1356	0.1367
	11	0.1370	0.1402	0.1324	0.1320	0.1360	0.1359	0.1367

^aNonrelativistic calculation with the Levy-Leblond Hamiltonian. ^bWith truncation of virtual orbitals on 100 au done by RELCCSD.

first singlet state. However, in both the correlation models B3LYP and CC, the first singlet state is positioned above the second triplet. To address this issue, we perform nonrelativistic calculations for the ten lowest states, including five triplets and five singlets. Detailed results are provided in the [Supporting Information](#). Similar to I_2 , we note that the CIS largely overcomes the triplet instability seen in HF and yields a more systematic error pattern when compared to B3LYP and CC.

6. CONCLUSIONS

In this work, we describe the formulation and implementation of the relativistic coupled cluster linear response method for static and frequency-dependent molecular property calculations that can accurately treat both relativistic and electronic correlation effects. This implementation was accomplished in the GPU-accelerated coupled cluster module of the DIRAC program, leveraging a framework designed to handle similar transformed Hamiltonians in subspace. This framework aids in solving both eigenvalue and linear system problems. The current code is capable of calculating excitation energies within the EOM-CCSD framework and computing the linear response function for both CC–CI and CC–CC type wave function models.

We have validated the implementation by assessing purely electric properties such as static and frequency-dependent polarizability for group IIB atoms (Zn, Cd, and Hg) and several diatomic molecules. Compared with previous HF linear response calculations, our current linear response calculation based on the relativistic coupled cluster approach offers notably improved accuracy. This enhancement is particularly evident in terms of relativistic corrections and correlation, bringing our results closer to the experimental data.

In this study, we also tested the indirect spin–spin coupling constant—a purely magnetic property—for the hydrogen halide series HX ($X = \text{F, Cl, Br, and I}$). Validation was performed by reproducing the results obtained by other programs such as DALTON and CFOUR using a nonrelativistic Hamiltonian. We extended our study to explore the impact of the solvent effect on the $\text{H}_2\text{Se–H}_2\text{O}$ complex systems. Both correlation and relativistic corrections were found to have pronounced effects on the solvent shift. While CC and DFT gave similar magnitudes for the shifts in the solvent effect, the absolute spin–spin coupling constants differed significantly. This finding calls for caution when DFT is employed for such calculations.

Lastly, we computed the optical rotation—an electric and magnetic mixed property—for chiral molecules H_2Y_2 ($Y = \text{O, S, Se, and Te}$) at the wavelength of sodium D-line (589.29 nm). Our exploration revealed potential challenges when using this frequency for heavy molecules. We analyzed the poles of the response function by calculating the excitation energy and advise caution when using sodium D-line for these heavier molecules in future investigations.

A distinguishing aspect of our implementation is its use of complex algebra, which facilitates a straightforward extension of real to complex frequencies for the evaluation of the damped linear response function. We used this feature to simulate the spectrum of I_2 through the assessment of the absorption cross-section.

As a final point and perspective, it is worth noting that our current implementation relies on the single-code tensor operation library TAL-SH. While efficient, this library is limited to using the memory capacity of a single node. Therefore, a natural development is to extend the current code for the EOM-CCSD energy and linear response to use a library suited for

distributed memory computing architectures, such as the ExaTensor library, already employed for the CC energy evaluation but still lacking some features needed in the Davidson diagonalization procedure. After resolving these issues, we are optimistic that we can eliminate the limitations caused by the library being able to use the memory of only a single compute node and enable treatment of larger systems.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jctc.3c00812>.

Working equations for CCSD linear response theory and EOM-EE sigma vectors and intermediates, comparison for the BH molecule of the damped response LR-CC results obtained with DIRAC and standard LR-CC results obtained with DALTON, indirect spin–spin coupling constants (J) for the hydrogen halide molecule, and additional comparisons of methods for optical rotation (PDF)

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Notes

The authors declare no competing financial interest. The data (input/output) corresponding to the calculations of this paper are available at the Zenodo repository under DOI:10.5281/zenodo.8136133.

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